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Visible photoluminescence in ZnO tetrapod and multipod structures

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The properties of ZnO tetrapod and multipod structures were investigated using scanning electron microscopy, x-ray diffraction, photoluminescence (PL), and electron paramagnetic resonance (EPR) spectroscopy. While there is relationship between $g=1.96$ EPR and green PL in some of the samples, this is not the case for all the samples. Therefore, the commonly assumed transition between a singly charged oxygen vacancy and photoexcited hole [K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, and J. A. Voigt, Appl. Phys. Lett. **68**, 403 (1996)] does not explain the green emission in all ZnO samples. The green emission likely originates from surface defects. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1695633]

ZnO is of great interest for photonic applications due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV). In the photoluminescence (PL) spectrum of ZnO, typically one UV peak can be observed due to band edge emission, and one or more peaks in the visible spectral range (usually broad green,[1–7] although blue[8] and red[9] peaks have also been reported) due to defect emission. The origin of the green emission is controversial and several mechanisms have been proposed.[1–7] Vanheusden *et al.*[1,2] explained the green emission as a transition between singly charged oxygen vacancy and photoexcited hole, based on the correlation between the green PL and electron paramagnetic resonance (EPR) peak at $g\approx 1.96$. It was also proposed that green emission in ZnO originates from Cu impurities,[3,4] and donor–acceptor and shallow donor-deep level transitions.[5–7] Garces *et al.*[3] proposed that the structured green emission (after high-temperature annealing) is associated with Cu^{2+} ions, while unstructured emission observed before annealing is due to the donor–acceptor transition involving Cu^{+} acceptors. However, if the green emission in ZnO samples is due to impurity rather than intrinsic defects, it is not expected that the emission intensity would be dependent on the fabrication atmosphere as reported previously.[10] Also, the variation of the peak positions with different annealing conditions,[11,12] and measured at different temperatures[12] may be more consistent with an intrinsic defect than an extrinsic impurity.

In this work, we performed EPR and PL measurements for pure ZnO samples prepared either from oxidation of Zn in air as reported previously[10] or by heating a mixture of ZnO and graphite (1:1) at 1100 °C in a tube furnace. We also fabricated ZnO samples by heating a mixture of ZnO, GeO_2, and graphite at 1100 °C in order to modify the morphology of the fabricated structures. The percentage of GeO_2 was 2.5%, 5%, and 10%. In all cases, white deposition products were obtained on the walls of the tube. The structure of deposited materials was investigated by x-ray diffraction (XRD) using Siemens D5000 x-ray diffractometer, x-ray fluorescence (XRF) using a XRF spectrometer JEOL JSX-3201Z, energy dispersive x-ray spectroscopy (EDX) using Link Analytical eXL, scanning electron microscopy (SEM) using Cambridge-440 SEM, and transmission electron microscopy (TEM) and selected area electron diffraction (SAED) using Philips Tecnai 20 TEM. The room-temperature PL was measured using a HeCd laser excitation source (325 nm). For investigating whether the emission originates from surface defects, fabricated nanostructures were coated with a surfactant using the following procedure. ZnO tetrapod/multipod nanostructures were dispersed in a dichloromethane solution of *n*-hexyltrichlorosilane in an ultrasonic bath for 1 h. After dispersion, nanostructures were separated using centrifuge and rinsed thoroughly with dichloromethane to remove any residual surfactant and dried in an oven.

Figure 1 shows the representative SEM images of the obtained ZnO structures. Similar tetrapod structures are obtained for both starting materials (Zn and ZnO:C). When GeO_2 is added to the starting material (ZnO:C), multipod structures are formed, as illustrated in Fig. 1(c). With increasing GeO_2 concentration in the starting material, larger amount of multipod structures are formed (for small GeO_2 content, sample contains tetrapods and multipods). In order to determine Ge content in deposited material, we performed XRF measurements of the bulk quantity powder and examined individual multipod structures using EDX spectroscopy. XRF found small (<1 mol %) quantity of Ge in some of the samples, but there was no relationship between Ge concen-

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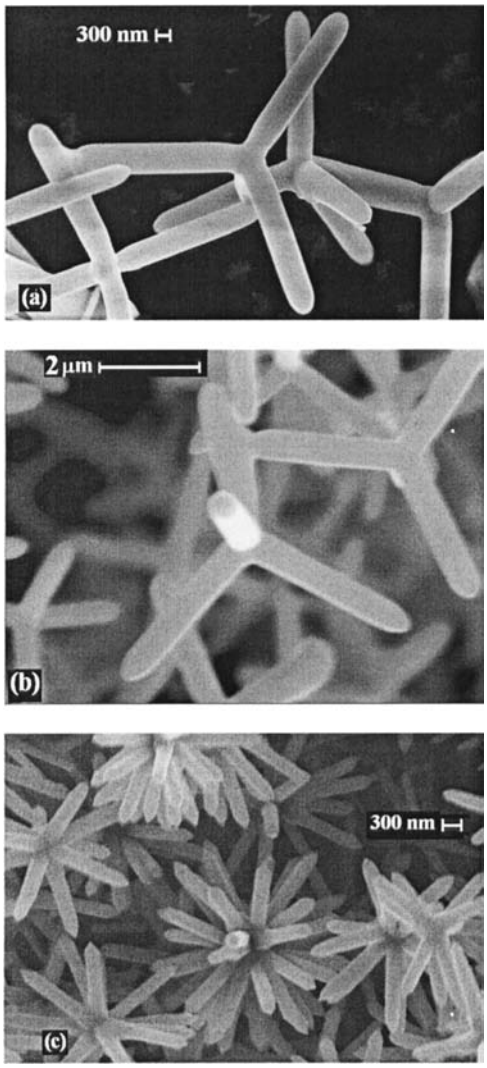

FIG. 1. Representative SEM images of ZnO nanostructures: (a) ZnO prepared from Zn, (b) ZnO prepared from ZnO:C, and (c) ZnO prepared from ZnO:C:GeO_2.

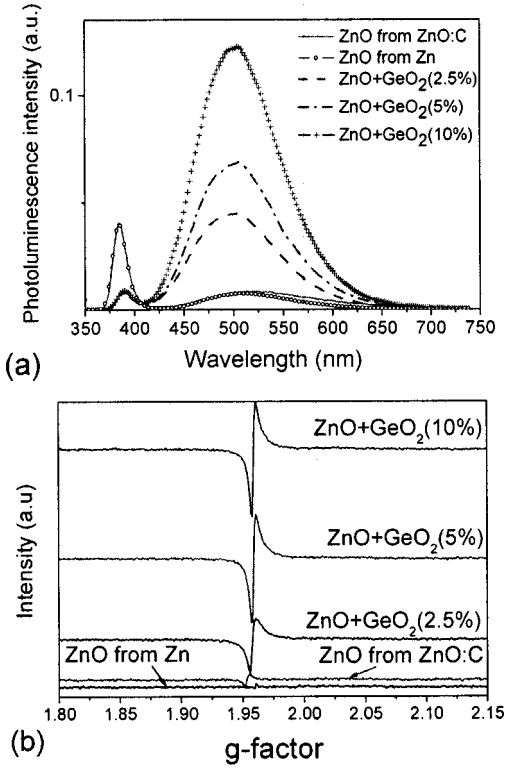

FIG. 2. (a) PL spectra and (b) EPR spectra measured at room temperature from ZnO structures prepared from different materials. EPR spectra have been vertically shifted for clarity.

tration determined by XRF and GeO_2 content in the starting material. EDX detected no Ge in the majority of the multipod structures. Therefore, we can conclude that Ge enables nucleation of additional legs on the core which would normally develop into a tetrapod, but it is not incorporated in the multipod structure in significant concentration. In XRD spectra, only the peaks corresponding to hexagonal ZnO are detected in all samples.

We performed PL and EPR measurements. The obtained results are shown in Fig. 2. All samples show UV and broad green emission peaks. Since the samples are in the powder form, the ratio of UV to green emission should be compared instead of the absolute PL intensity which is dependent on the quantity of the powder excited by the laser beam. The pure ZnO samples have very similar PL spectra, while the samples prepared from a ZnO:C:GeO_2 mixture show very strong green PL where green peak intensity increases with the increase of GeO_2 concentration in the starting material. The same trend (increase in the intensity with increased GeO_2 concentration in the starting material) can also be observed for EPR $g \approx 1.96$ peak. However, the sample fabricated by oxidation of Zn does not show a clear EPR $g \approx 1.96$ peak (signal at $g \approx 1.96$ is practically at noise level). A broad weak feature between $g \sim 2.007$ and $g \sim 2.05$, attributed to chemisorbed oxygen,[13] can also be barely observed in the freshly prepared sample from Zn (but it becomes stronger with atmosphere exposure). The EPR $g \approx 1.96$ peak is typically assigned to shallow donors,[3,14,15] and the signal has the same position regardless of the nature of the shallow donor.[15] This signal has been previously assigned to singly ionized oxygen vacancies V_o^+.[1,2,14] However, this assignment is controversial. It was also reported that V_o^+ produces EPR signal $g_\perp = 1.9945$ and $g_\parallel = 1.9960$.[3,15,16] Possible native shallow donors in ZnO are oxygen vacancies and interstitial zinc Zn_i. According to recent theoretical calculations,[17] the native shallow donor may be Zn_i, while the oxygen vacancy is a deep donor. Therefore, it is possible that $g \approx 1.96$ signal is due to interstitial zinc.

Regardless of the origin of the EPR peak, it can be concluded that, in the general case, there is no relationship between this signal and green PL. Green PL is present even when there is no significant EPR signal at $g \approx 1.96$. The ZnO tetrapods fabricated from Zn and ZnO:C show very similar PL spectra (the green peak for ZnO from Zn shows ~50 meV blueshift), while only tetrapods fabricated from ZnO:C show a $g \approx 1.96$ signal. It is possible that in the former case, the green emission originates from a transition between the electron in the conduction band and the deep level while, in the latter case, the transition between shallow donor and deep acceptor is observed. The former hypothesis is in agreement with the luminescence mechanism proposed by Van Dijken *et al.*[18,19] involving an electron in a conduction band and deeply trapped hole. The latter mechanism is in agreement with a proposed explanation for green luminescence involving donor–acceptor transitions.[5–7] Recent ex-

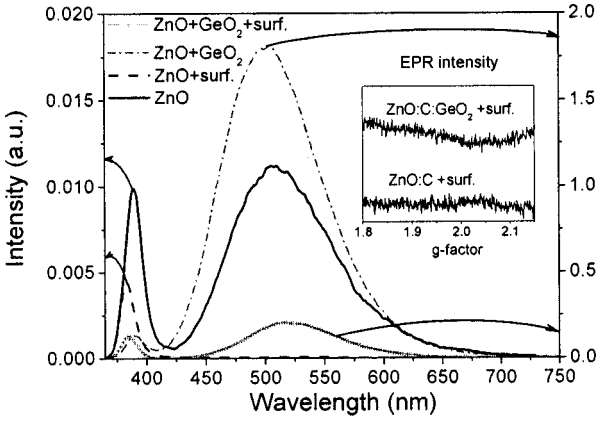

FIG. 3. Effects of surfactant on PL from ZnO and ZnO:Ge nanostructures. The inset shows EPR spectra (vertically shifted for clarity) with a surfactant.

periments on the influence of the electric field to the green luminescence in ZnO single crystals indicate that the luminescence may be due to complex defects including Zn_i,[20] so that it is possible that the green luminescence in the samples fabricated from ZnO:C is from the transition between zinc interstitials and the deep acceptor level.

Samples fabricated with the addition of GeO_2 to the starting material exhibit strong enhancement of the $g \approx 1.96$ EPR signal and green PL. The samples fabricated with GeO_2 in the starting material exhibit a slight shift ($\Delta g = 0.004$) of the EPR signal, as well as a 5 nm redshift of the UV PL peak, and an ~10 nm blueshift of the green PL compared to samples fabricated from ZnO:C mixture without the addition of GeO_2. Since no Ge was detected in the majority of multipod structures examined by EDX, it is possible that the obtained morphologies in the presence of GeO_2 in the starting material contain different types of intrinsic defects or have strain due to their peculiar morphology. It should also be observed that the fabricated multipod structures have a very large surface area, and that the increase in the surface area may account for the increase in green PL if the defects responsible for this emission are mainly located at the surface. To test this hypothesis, we performed PL and EPR measurements on ZnO structures coated with a surfactant. The results are shown in Fig. 3. It can be observed that the presence of the surfactant significantly reduces green PL intensity both in ZnO tetrapods (pure ZnO) and ZnO multipods. This indicates that the green luminescence mainly originates from the surface. This is in agreement with the hypothesis that visible PL in ZnO nanoparticles originates from surface centers.[21] Surfactant coating also reduces EPR signal intensity both in ZnO structures fabricated from ZnO:C and $ZnO:C:GeO_2$, which agrees with the reported reduction of EPR peak intensity in ZnO nanoparticles coated with a surfactant.[22] This result is in agreement with the fact that the surface concentration of intrinsic defects is larger than the bulk defect concentration.[23]

To summarize, we have performed PL and EPR spectroscopy studies of ZnO structures fabricated from different starting materials. We found that, while there is a correlation between EPR peak intensity and green PL intensity in some samples, this is not the case for all the samples. The obtained results indicate that the green PL is due to transition between a shallow donor and deep acceptor in the presence of $g \approx 1.96$ EPR signal and transition between the conduction band and deep acceptor in the absence of $g \approx 1.96$ EPR signal. From the effects of coating the fabricated structures with a surfactant, it can be concluded that the defects responsible for green PL are mainly located at the surface.

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